PATENT SPECIFICATION 1,007,172

NO DRAWINGS

1,007,172

Date of Application and filing Complete Specification:
June 18, 1962. *No. 23413/62.*

Application made in Hungary (No. 133) on July 1, 1961.
(Patent of Addition to No. 992,118, dated July 19, 1961.

Complete Specification Published: Oct. 13, 1965.

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Int. Cl.:—C 01 b, f, g /C 09 d.

COMPLETE SPECIFICATION.

Process for the Preparation of Organophilic Pigments.

PATENTS ACT, 1949

SPECIFICATION NO. 1,007,172

In accordance with the Decision of the Superintending Examiner, acting for the Comptroller-General, dated the fifth day of January 1967 this Specification has been amended under Section 29 in the following manner:-

Page 1, line 64, and Page 5, line 38, *delete* "an" *insert* "a simple"

Page 1, line 65, *after* "particles." *insert* "By the term "simple aqueous suspension" we mean a suspension which contains no added dispersing agents."

Page 5, line 38, *after* "suspension" *insert* ", as herein defined,"

THE PATENT OFFICE,
15th February, 1967 D 80567/10

ERRATUM

SPECIFICATION NO. 1,007,172

Page 4, line 95, *for* ""Hansa yelloy"" *read* ""Hansa yellow""

THE PATENT OFFICE,
22nd February, 1967 D 80614/1

introduced into the solution whereby the and have no covering power.

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Int. Cl.:—C 01 b, f, g /C 09 d.

COMPLETE SPECIFICATION.

Process for the Preparation of Organophilic Pigments.

We, LAJOS CSONKA of 14, Pazsit utca, Budapest II; JANOS SZERECZ of 35a Csalan utca, Budapest II; FERENC HORKAY of 4, Kapitany utca, Budapest XII; FERENC SZANTO of 6 Corvin utca, Budapest IV; GEZA SZEKELY of 18 Kossuth Lajos ter, Budapest V; and JENO GONCZY of 34, Csalan utca, Budapest II, all of Hungary, all Hungarian citizens, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with an improvement in or modification of the invention the subject of Patent Application No. 992,118.

In Patent Application No. 992,118 there is described a process for the preparation of organophilic sulphate, carbonate and phosphate pigments in which an aqueous suspension of the pigment is reacted in the presence of one or more zinc or aluminium oxides, oxide hydroxides or hydroxides with an anionic surface active agent having an apolar radical, the precipitate so formed is separated from the aqueous liquid, washed if desired, thereafter dried and then disintegrated if desired.

It has been observed that due to chemisorption, the anionic surface active agents having an apolar radical are adsorbed by the surface of the pigments. Thus ions are introduced into the solution whereby the pigments are peptized; consequently, both the filterability and the colour of the pigments are impaired.

It has now been found that certain other pigments and similar materials, described more fully below, may be rendered organophilic by the process described in Patent Application No. 992,118.

According to the invention, therefore, there is provided a process for rendering readily dispersible in organic media a hydrophilic substance selected from:—

(a) oxide, chromate, sulphide, cyanide, antimonate, selenide and vanadate inorganic pigments;
(b) azo and phthalocyanine organic pigments; and
(c) filling materials as herein defined;

in which an aqueous suspension of said hydrophilic substance is reacted in the presence of one or more amphoteric oxides, oxide hydroxides or hydroxides of zinc, aluminium, lead or chromium with an aqueous solution of an anionic surface active agent having an apolar grouping to provide an organophilic coating on the surface of said substance, and the resultant precipitate is separated from the reaction mixture, washed, if desired, and thereafter dried and, if desired, finely divided into small particles.

The term "filling material" is a term of the art and refers conventionally to pigments which after incorporation into organic vehicles do not colour the organic vehicle and have no covering power.

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Suitable amphoteric oxides for use in the process according to the invention are zinc oxide (ZnO) and aluminium oxide [Al_2O_3]; a suitable amphoteric oxide hydroxide is aluminium oxide hydroxide [AlO(OH)] and suitable amphoteric hydroxides include aluminium hydroxide [$Al(OH)_3$], lead hydroxide [$Pb(OH)_2$] and chromium hydroxide [$Cr(OH)_3$].

Examples of anionic surface active agents having an apolar grouping which may be used are alkali metal or ammonium salts of saturated, unsaturated and substituted fatty acids having at least 8 carbon atoms, e.g. sodium stearate, ammonium palmitate and sodium ricinoleate; alkali metal or ammonium salts of industrial stearine containing stearic, palmitic and oleic acids; alkali metal or ammonium salts of polymerized unsaturated fatty acids, e.g. the sodium or ammonium salts of boiled linseed oil; alkali metal or ammonium alkyl, aryl or mixed alkyl-aryl sulphonates and sulphates; and alkali metal or ammonium salts of alkyl, aryl or mixed alkyl-aryl phosphoric or polyphosphoric acids.

The essence of the process according to the invention is that the large organic anions having a charge opposed to that of the surface of the pigment are orientedly adsorbed at the so-called active sites of the surface of the pigment particles, these anions being irreversibly bound by electrostatic forces so that the apolar groups of the asymmetrically polar organic ions are oriented outwards from the surface of the pigment particles, thus providing an organophilic coating at the surface of the pigment particles. The hydroxide ions formed by the hydrolysis of the anionic surface active agents are bound by the amphoteric oxides, oxide hydroxides or hydroxides. Consequently, the particles are coagulated and precipitated in the suspension. During drying the surface layer having an oriented structure is practically irreversibly bound to the particles and thus the surface of the pigment or filling material is rendered permanently organophilic. This means that pigments which could originally be wetted by water, when treated with the process according to the invention become pigments which can be easily wetted by organic media such as aliphatic and aromatic hydrocarbons, ketones, alcohols, esters and ethers.

The process according to the invention is preferably carried out using a 2—65% by weight aqueous suspension of the freshly precipitated or finely ground, possibly washed hydrophilic material to which the amphoteric oxides, oxide hydroxides or hydroxides are added, preferably in an amount of 0.1 to 4% by weight based on the weight of hydrophilic substance. The suspension is stirred and then reacted with the aqueous solution of the anionic surface active agent which preferably contains from 1 to 5% by weight of surface active agent, at an elevated temperature, e.g. 70 to 80°C. The amount of the anionic surface active agent employed can be varied, depending on the grade of dispersity of the hydrophilic substances, and is preferably from 0.1 to 15%, by weight based on the weight of hydrophilic substance. The pigment suspension obtained may then be filtered, washed if desired, dried, and finally disintegrated if desired.

Organic suspensions of hydrophilic substances rendered organophilic by the process according to the invention may be used as or in printing inks, oil or oleoresinous paints or varnishes and give little or no sediment even on standing for a long time. Thus very little or no wetting agents or anti-sedimentation agents are needed. Filling materials rendered organophilic by the process according to the invention may be used to render organophilic and thereby stabilize minor quantities of non-organophilic pigments.

Grinding, or subdivision, of particles of hydrophilic substances treated by the process of the invention may be effected using considerably less energy than in the case of untreated particles and further the tendency to form aggregates on storage is diminished, and stable organic suspensions may be obtained. Layers or films of organophilic substances prepared by the process of the invention are substantially uniform, and their water resistance, weather-proofness as well as their physical and chemical resistivity are improved. Due to good solvation of the particles, the lightness of films or varnishes prepared using these organophilic substances is, in general, better than that of the untreated pigments, and the covering power of the varnishes or paints is also improved.

In order that the invention may be well understood the following examples are given by way of illustration only.

Example 1

500 g of titanium dioxide [TiO_2] and 1 g of aluminium hydroxide [$Al(OH)_3$] are suspended in 2 litres of water. With strong stirring 1 litre of a 1% ammonium stearate solution is added at a temperature of 60—80°C. After a quarter of an hour the precipitated substance is filtered, washed with water and dried at 105°C. The hydrophobic titanium dioxide thus obtained can be easily crumbled; consequently, when triturated into paints, the paints do not become chalky, this phenomenon being always observable in case of the non-organophilized titanium dioxide pigments.

Example 2

One proceeds as described in Example 1, except as follows:

(a) Instead of the 1% solution of ammonium stearate, a 0.5% solution of the sodium salt of a polymerized fatty acid, boiled linseed oil, is used.

(b) Instead of the 1% solution of ammonium stearate, a 1% solution of ammonium ricinoleate is used.

(c) Instead of the 1% solution of ammonium stearate, 150 ml of a 5% solution of sodium cetyl sulphonate is used.

Example 3

One proceeds as described in Examples 1 or 2, except as follows:

(a) Instead of the titanium dioxide, yellow iron oxide is used.

(b) Instead of the titanium dioxide, red iron oxide is used.

(c) Instead of the titanium dioxide, black iron oxide is used.

(d) Instead of the titanium dioxide, bauxite red is used.

Example 4

One proceeds as described in Examples 1 or 2, but instead of the titanium dioxide, chrome oxide green [Cr_2O_3] and instead of the aluminium hydroxide, chromic hydroxide ($Cr[OH]_3$) are employed.

Example 5

500 g of minium [Pb_3O_4] and 1 g of lead hydroxide [$Pb(OH)_2$] are suspended in 2 litres of water. With strong stirring, 200 ml of a 1% solution of ammonium stearate are added at a temperature of 60—80°C. After 15 minutes the precipitate is filtered, washed with water, dried until free from water and triturated in an edge runner. The minium thus obtained has hydrophobic properties, it can be easily crumbled, and when milled into alkyd resins it does not cause gelation even after several months; on the contrary, untreated minium milled into alkyd resins causes gelation with 1 to 2 days, whereby the paint becomes unusable.

Example 6

500 g of barium chromate [$BaCrO_4$] and 1 g of aluminium oxide hydroxide (AlO[OH]) are suspended in 2 litres of water, then with strong stirring a 1% solution of 4 g ammonium stearate is added at a temperature of 60 to 70°C. The precipitated substance is filtered, dried at 105°C until free from water and finally disintegrated.

Example 7

One proceeds as described in Example 6 except as follows:

(a) Instead of the 1% solution of ammonium stearate, a 1% solution of the sodium salt of caprylic acid is used.

(b) Instead of the 1% solution of ammonium stearate, a 1% solution of ammonium ricinoleate is used.

(c) Instead of the 1% solution of ammonium stearate, a 1.5% solution of the sodium salt of perlargonic acid is used.

(d) Instead of the 1% solution of ammonium stearate, a 2% solution of sodium cetyl phosphate is used.

(e) Instead of the 1% solution of ammonium stearate, a 1% solution of the sodium salt of a polymerized fatty acid, boiled linseed oil, is used.

Example 8

One proceeds as described in Examples 6 or 7 except as follows:

(a) Instead of barium chromate, strontium chromate is used.

(b) Instead of barium chromate, zinc chromate is used.

(c) Instead of barium chromate, lead chromate is used.

Example 9

0.5 g of aluminium hydroxide ($Al[OH]_3$) is added to 1000 g of a 5% suspension of freshly precipitated Berlin blue, washed free from ions. With strong stirring 100 g of a 2.5% solution of ammonium stearate is added at 65 to 80°C. The precipitated substance is filtered and dried at a temperature ranging from 60 to 120°C until free from water.

The dried product is a hydrophobic pigment which can be easily milled and excellently wetted by organic media of apolar and slightly polar character.

Example 10

One proceeds as described in Example 9 except as follows:

(a) Instead of the 2.5% solution of ammonium stearate, a 2% solution of ammonium laurate is used.

(b) Instead of the 2.5% solution of ammonium stearate, a 2% solution of sodium dicetyl pyrophosphate is used.

Example 11

500 g of finely ground cadmium sulphide [CdS] and 0.8 g. of aluminium hydroxide ($Al[OH]_3$) are suspended in 2 litres of water. With strong stirring 200 g of a 2% aqueous solution of ammonium stearate are added at a temperature of 60 to 80°C.

The pigment, which is precipitated in an easily filterable form, is filtered, washed if desired, then dried at a temperature ranging from 80 to 120°C until free from water and finally disintegrated.

The product thus obtained is a pigment of hydrophobic character which can be excellently wetted in organic media of apolar and slightly polar character.

Example 12

One proceeds as described in Example 11 except as follows:

(a) Instead of the 2% solution of ammonium stearate, a 1.5% solution of ammonium laurate is used.

(b) Instead of the 2% solution of ammonium stearate, a 2.5% solution of sodium cetyl phosphate is used.

(c) Instead of the 2% solution of ammonium stearate, a 2% solution of the sodium salt of cetyl naphthalene sulphonic acid is used.

Example 13

One proceeds as described in Examples 11 or 12 except as follows:

(a) Instead of cadmium sulphide, arsenic sulphide is used.

(b) Instead of cadmium sulphide, antimony sulphide is used.

(c) Instead of cadmium sulphide, tin sulphide is used.

(d) Instead of cadmium sulphide, mercury sulphide is used.

(e) Instead of cadmium sulphide, cadmium sulphide selenide is used.

(f) Instead of cadmium sulphide, zinc sulphide is used.

Example 14

500 g of cobalt violet ($CoO_2[PO_4]_2$) and 2 g of zinc hydroxide ($Zn[OH]_2$) are suspended in 2 litres of water. With strong stirring 600 g of a 1% solution of ammonium ricinoleate are added. The precipitate obtained is filtered, dried at 60 to 100°C and disintegrated.

Example 15

500 g of Naples yellow (lead antimonate: $Pb_3[SbO_4]_2$) and 1 g of zinc hydroxide ($Zn[OH]_2$) are suspended in 2 litres of water, and with strong stirring 200 g of a 4% solution of sodium cetyl sulphonate are added. The precipitate is filtered, dried and finally disintegrated.

Example 16

500 g of molybdic red [x PbO. $PbCrO_4$ + y $PbMoO_4$ + z $PbSO_4$] and 1.5 g of zinc hydroxide ($Zn[OH]_2$) are suspended in 2 litres of water. With strong stirring 200 g of a 5% solution of sodium cetyl sulphonate are added at 65°C. The precipitate obtained is filtered, dried at 80°C and finally disintegrated.

Example 17

500 g of "Hansa yellow" ("Hansa" is a registered Trade Mark) prepared by reacting *m*-nitro-*p*-toluidine with acetyl acetanilide are suspended together with 1 g of aluminium hydroxide in 2 litres of distilled water. Under strong stirring 1 litre of a 1% solution of ammonium stearate is added at 60 to 80°C. The organic pigment precipitates from the aqueous suspension in flocculent form. The precipitate is filtered, washed with water and dried until free from water. After drying the pigment has hydrophobic properties, and it can be excellently wetted by organic media of slightly polar or apolar character.

Example 18

One proceeds as described in Example 17 except as follows:

(a) Instead of the 1% solution of ammonium stearate, a 1% solution of ammonium ricinoleate is used.

(b) Instead of the 1% solution of ammonium stearate, 150 ml. of a 3.5% solution of sodium cetyl sulphonate is used.

(c) Instead of the 1% solution of ammonium stearate, a 1% solution of the sodium salt of caprylic acid is used.

(d) Instead of the 1% solution of ammonium stearate, a 2% solution of sodium cetyl phosphate is used.

Example 19

One proceeds as described in Examples 17 to 18 except as follows: :

(a) Instead of the "Hansa yellow", "permanent red" prepared by reacting *o*-chloro-*p*-nitraniline with beta-naphthol is employed.

(b) Instead of the "Hansa yellow", "benzidine yellow" [permanent yellow] prepared by reacting dichlorobenzidine with acetyl-aceto-*m*-xylidine is employed.

(c) Instead of the "Hansa yelloy", "benzidine orange" [permanent orange] prepared by reacting dichloro benzidine with phenyl methyl pyrazolone is used.

(d) Instead of the "Hansa yellow", "Helio red RMT extra" prepared by reacting *m*-toluidino-*o*-sulphonic acid with beta-naphthol is employed.

(c) Instead of the "Hansa yellow", "benbordeaux BL" prepared by reacting α-naphthoylamine with 1-naphthol-5-sulphonic acid is used.

(f) Instead of the "Hansa yellow", "permanent bordeaux FRE" prepared by reacting *m*-nitro-*o*-toluidine and beta-oxynaphthoyl-*o*-toluidine is used.

Example 20

500 g of phthalocyanine blue [Heliogen blue B] and 0.8 g of chromic hydroxide ($Cr[OH]_3$) are suspended in 2 litres of water. ("Heliogen" is a registered Trade Mark). With strong stirring 1200 ml of a 1% solution of ammonium stearate are added to 60 to 80°C. The organic pigment precipitates from the aqueous suspension in flocculent form. The pigment is filtered, washed with water and dried until free from water. The paint thus obtained is hydrophobic, it can be excellently

wetted by organic media of slightly polar or apolar character, and it no longer has a tendency to crystallization.

Example 21

One proceeds as described in Example 20 except as follows:

(a) Instead of the 1% solution of ammonium stearate, a 1% solution of the sodium salt of pelargonic acid is used.

(b) Instead of the 1% solution of ammonium stearate, a 1% solution of the sodium salt of a polymerized fatty acid, boiled linseed oil, is used.

(c) Instead of the 1% solution of ammonium stearate, a 1% solution of sodium dicetyl pyrophosphate is used.

(d) Instead of the 1% solution of ammonium stearate, a 1.5% solution of the sodium salt of cetyl naphthalene sulphonic acid is used.

Example 22

One proceeds as described in Examples 20 or 21 but instead of the phthalocyanine blue, phthalocyanine green ["Heliogen green G"] is employed.

WHAT WE CLAIM IS:—

1. A process for rendering readily dispersible in organic media a hydrophilic substance selected from:—
   (a) oxide, chromate, sulphide, cyanide, antimonate, selenide and vanadate inorganic pigments;
   (b) azo and phthalocyanine organic pigments; and
   (c) filling materials as herein defined;
in which an aqueous suspension of said hydrophilic substance is reacted in the presence of one or more amphoteric oxides, oxide hydroxides or hydroxides of zinc, aluminium, lead or chromium with an aqueous solution of an anionic surface active agent having an apolar grouping to provide an organophilic coating on the surface of said substance, and the resultant precipitate is separated from the reaction mixture, washed, if desired, and thereafter dried.

2. A process as claimed in claim 1 in which the dried precipitate is subsequently subdivided into small particles.

3. A process as claimed in claim 1 or claim 2 in which said amphoteric oxide is zinc or aluminium oxide.

4. A process as claimed in claim 1 or claim 2 in which said amphoteric oxide hydroxide is aluminium oxide hydroxide.

5. A process as claimed in claim 1 or claim 2 in which said amphoteric hydroxide is zinc or aluminium hydroxide.

6. A process as claimed in any of the preceding claims in which said anionic surface active agent is an alkali metal or ammonium salt of a saturated, unsaturated or substituted fatty acid containing at least 8 carbon atoms.

7. A process as claimed in claim 6 in which said anionic surface active agent is an alkali metal or ammonium salt of industrial stearine.

8. A process as claimed in claim 6 in which said anionic surface active agent is an alkali metal or ammonium salt of a polymerized unsaturated fatty acid.

9. A process as claimed in any of claims 1 to 5 in which said anionic surface active agent is an alkyl, aryl or mixed alkyl-aryl sulphonate or sulphate.

10. A process as claimed in any of claims 1 to 5 in which said anionic surface active agent is an alkali metal or ammonium salt of an alkyl, aryl or mixed alkyl-aryl phosphoric or polyphosphoric acid.

11. A process as claimed in any of the preceding claims in which the reaction between the aqueous suspension of the hydrophilic substance and the aqueous solution of the anionic surface active agent is effected at a temperature of from 70 to 80°C.

12. A process as claimed in any of the preceding claims in which said aqueous suspension of hydrophilic substance contains from 2 to 65% by weight of said hydrophilic substance.

13. A process as claimed in any of the preceding claims in which said amphoteric oxide, oxide hydroxide or hydroxide is employed in an amount of from 0.1 to 4% by weight, based on the weight of hydrophilic substance.

14. A process as claimed in any of the preceding claims in which said aqueous solution of anionic surface active agent contain from 1 to 5% by weight of said anionic surface active agent.

15. A process as claimed in any of the preceding claims in which said anionic surface active agent is employed in an amount of from 0.1 to 15% by weight based on the weight of hydrophilic substance.

16. A process as claimed in claim 1 substantially as herein described with reference to any of the Examples.

17. A substance selected from:—
   (a) oxide, chromate, sulphide, cyanide, antimoniate, selenide and vanadate inorganic pigments;
   (b) azo and phthalocyanine organic pigments; and
   (c) filling materials as herein defined;
when rendered readily dispersible in organic media by a process as claimed in any of the preceding claims.